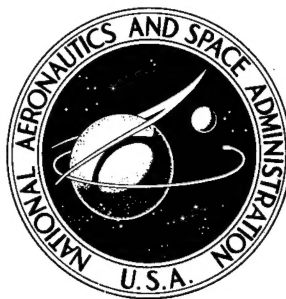


NASA TECHNICAL NOTE



NASA TN D-6983

NASA TN D-6983

CONFIDENTIAL
Approved for public release
Distribution Unlimited

ADHESION AND TRANSFER OF POLYTETRAFLUOROETHYLENE TO METALS STUDIED BY AUGER EMISSION SPECTROSCOPY

by *Stephen V. Pepper and Donald H. Buckley*

Lewis Research Center

Cleveland, Ohio 44135

19960425 070

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • OCTOBER 1972

DTIC QUALITY INSPECTED 1

18204

1. Report No. NASA TN D-6983		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle ADHESION AND TRANSFER OF POLYTETRAFLUOROETHYLENE TO METALS STUDIED BY AUGER EMISSION SPECTROSCOPY				5. Report Date October 1972	
				6. Performing Organization Code	
7. Author(s) Stephen V. Pepper and Donald H. Buckley				8. Performing Organization Report No. E-6897	
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135				10. Work Unit No. 502-01	
				11. Contract or Grant No.	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546				13. Type of Report and Period Covered Technical Note	
				14. Sponsoring Agency Code	
15. Supplementary Notes					
16. Abstract <p>The adhesion and transfer of polytetrafluoroethylene (PTFE) to metals in ultrahigh vacuum have been studied by using Auger emission spectroscopy. The transfer was effected both by compressive static contact and by sliding contact. The transfer observed after static contact was independent of the chemical constitution of the substrate. Electron-induced desorption of the fluorine in the transferred PTFE showed that the fluorine had no chemical interaction with the metal substrate. The coefficient of friction on metals was independent of the chemical constitution of the substrate. However, sliding PTFE on soft metals, such as aluminum, generated wear fragments that lodged in the PTFE and machined the substrate.</p>					
17. Key Words (Suggested by Author(s)) Teflon Adhesion Polytetrafluoroethylene Transfer Auger emission spectroscopy				18. Distribution Statement Unclassified - unlimited	
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 22	
				22. Price* \$3.00	

* For sale by the National Technical Information Service, Springfield, Virginia 22151

ADHESION AND TRANSFER OF POLYTETRAFLUOROETHYLENE TO METALS STUDIED BY AUGER EMISSION SPECTROSCOPY

by Stephen V. Pepper and Donald H. Buckley

Lewis Research Center

SUMMARY

The adhesion and transfer of polytetrafluoroethylene (PTFE) to metal substrates in ultrahigh vacuum (10^{-10} torr) has been studied by using Auger emission spectroscopy (AES). The experiments were performed with PTFE pins and metal disks. The PTFE was brought into both static and sliding contact with tungsten, tantalum, iron, aluminum, nickel, and copper disks, as well as tungsten disks that had been plated with silver and gold. During sliding the wear track on the disk was monitored with AES, and the friction force on the pin was measured.

The PTFE pin was placed in static contact with both atomically clean (argon ion sputtered) and oxidized metal surfaces. Examination of the contact spot on the disk with AES after removal of the pin revealed the presence of PTFE on all disks, including the silver and gold films, whether the surfaces were atomically clean or oxidized. The adhesion appears unrelated to the chemical activity of the metals and suggests a general van der Waals type of bonding interaction.

AES detected a transfer film of PTFE on the rotating metal surface during the initial revolution of the disk. The film was uniform across the track and only a few monolayers thick. The electron beam (2000 eV, 30 to 70 μ A) that excites the Auger transitions rapidly desorbs the fluorine in the PTFE film, while the carbon remains on the surface. This indicates that the fluorine in the film has no ionic or covalent type of chemical interaction with the metal substrate.

The coefficient of friction of PTFE on atomically clean tungsten (load, 250 g; sliding velocity, 0.07 cm/sec) was found to be 0.08. The second traversal on the track of the disk yielded the same coefficient of friction. The friction of PTFE proceeds independently of the chemical constitution of the substrate and is consistent with the lamellae-drawing picture of the sliding of PTFE.

The mechanical strength of the substrate, however, can be decisive in affecting the sliding behavior of PTFE. PTFE sliding on either an atomically clean or oxidized surface of aluminum in vacuum produces wear fragments of aluminum that lodge in the softer pin and serve to actually "machine" the metal disk.

INTRODUCTION

The polytetrafluoroethylene (PTFE)-metal interface has been a system of interest for many years. This interest has been generated by the unusual physical and chemical properties of PTFE itself. The low friction and wear characteristics of PTFE have found applications in bearing surfaces with metal parts, while the chemical inertness has made it attractive for corrosive media. Its low bulk strength has usually made it necessary to support a PTFE film by bonding it to a metal substrate. To understand the low friction as well as the adhesion (or lack of it) of PTFE, knowledge of the PTFE-metal interface is necessary.

It is the objective of this report to introduce a new technique, namely, Auger emission spectroscopy (AES) (ref. 1), into the study of the adhesion and friction of the PTFE-metal interface. This technique uses electron spectroscopy of metal surfaces in ultrahigh vacuum to identify the elements heavier than helium present in the top three layers. The advantages of this technique are (1) oxide films, surface contaminants, and transferred species can be unambiguously identified; (2) the technique is sensitive to concentrations less than one monolayer (0.01 monolayer); (3) the ultrahigh-vacuum chamber provides a highly controlled environment for both the generation of atomically clean surfaces and their deliberate contamination with selected gases; (4) the electron beam that excites the Auger transitions can desorb surface species and leads to additional information on the interaction between the adsorbate and the metal surface.

In this study results were obtained for both static and sliding contact of PTFE on metal surfaces. The object of the experiments was to assess the effect of chemical constitution of the mating surface and ambient environment on the adhesion and friction of PTFE. The metal surfaces were both atomically clean and deliberately oxidized. AES was used to characterize chemically the metals prior to contact and to observe transferred PTFE after contact.

The static experiments were designed to test for adhesion between PTFE and metal by detecting the presence of PTFE on the metal after the contact. The detection of transferred polymer is also of interest in the tensile and peel testing of adhesive joints. In this case the locus of failure of the joint is determined by examination of the fracture surfaces for the presence of transferred polymer. The sliding contacts extend the work of Makinson and Tabor on the PTFE-glass interface (ref. 2) to metal surfaces in general and atomically clean ones in particular. The coefficient of friction on these surfaces is obtained, and aspects of the transfer film on the surface are examined with AES.

BACKGROUND

The study of the PTFE-metal interface in the field of friction and wear has pro-

ceeded along the same lines taken in the study of friction and wear of metals. Thus, Makinson and Tabor (ref. 2) have slid PTFE balls on glass and studied the friction and transfer of PTFE to the glass. Steijn (ref. 3), on the other hand, has slid steel balls on abraded flats of PTFE and observed the drawing of polymer filaments over the grooves in the flats. In both these studies, the observation of the PTFE was made by microscopy (optical or electron), and a general conclusion from these sliding experiments was that the PTFE adhered to the material in contact with it, although there was uncertainty as to the strength of this adhesion.

There are two aspects of these experiments that bear refinement. First, the experiments were performed on surfaces that were characterized only in a crude sense. That is, they appeared clean by visual or electron microscopy or by the wetting criterion. However, it is well known that adhesion and friction can be quite sensitive to the chemical constitution of the surface. Proper identification of the oxide or contaminant films of monolayer thickness is therefore important (refs. 4 and 5). Certainly a better characterization of the contacting surface is desirable.

Second, the evidence for adhesion was inferred from the ability of the materials contacting the PTFE to draw films of it as a result of sliding contact. More direct evidence may be obtained from static contact, followed by inspection of the contacted surface for transferred material. This procedure is widely used in the fundamental investigation of adhesion, friction, and wear of metals. The technique, however, requires the detection of very small amounts of transferred material, amounts beyond the capabilities of the usual optical or electron microscopy.

It is thus of interest to extend the investigation of the friction and adhesion of PTFE with modern analytic methods capable of chemically characterizing surface species of fractional monolayer concentration. Then not only can the precontact surface chemistry be documented, but also the postcontact visual and microscopic observation of transferred species can be extended to fractional monolayer concentrations.

One such type of surface tool, the field ion microscope, has been used at the NASA Lewis Research Center to study the adhesion and transfer of PTFE to tungsten in static contact. In this technique, atomically clean and perfect metal tips may be produced, and the presence of fractional monolayer concentrations of foreign species detected. Evidence has been presented (ref. 6) for both adhesion and transfer of PTFE to tungsten that suggests a chemical bond can exist between the PTFE fragment and the metal surface. The possibility of chemical bonds between PTFE and clean metal opens up interesting lines of research both in the practical aspect of bonding PTFE to metal and for basic research on the friction of PTFE. The experiments with AES discussed in this report extend the field ion microscope work to both static and sliding contact on practical metal surfaces.

APPARATUS

The experimental apparatus has been described in reference 7 and is depicted in figure 1. The PTFE was in the form of a bullet with a radius of 0.476 centimeter (3/16 in.) at the contact end. The metals to be contacted were in the form of flat disks 6.35 centimeters (2.5 in.) in diameter. The PTFE contacted the disk about 2.54 centimeters (1 in.) from the center. The specimens were mounted in a stainless-steel vacuum chamber which was evacuated from atmospheric pressure by sorption pumps and then by an ion pump to an ultimate pressure of 1×10^{-10} torr. The chamber was bakeable to 250° C. The pressure was measured by a cold cathode discharge gage in the ultrahigh-vacuum ($< 1 \times 10^{-5}$ torr) region and by a hot-cathode ion gage in the low-vacuum region ($> 1 \times 10^{-5}$ torr).

The metal disk was mounted on a rotary magnetic feed-through that was either driven by a motor when the PTFE was in sliding contact or manipulated by hand for precise positioning of the disk following a static contact. The PTFE was supported by an arm that was mounted on a gimbal and sealed to the chamber with a bellows. A linkage at the end of the retaining arm farthest from the PTFE was connected to a strain gage assembly that was used to measure friction force. Load was applied by a deadweight loading system.

The surface of the disk was bombarded with 2000-volt electrons (30 to 70 μ A) from the coaxial electron gun. The energy of the secondary electrons emitted by the surface is analyzed by the cylindrical mirror electron spectrometer surrounding the electron gun (fig. 1(b)). The Auger electrons found in the secondary electron energy spectrum identify the elements heavier than helium present in the surface region to a depth of about three monolayers. The spectrometer analyzed a spot (< 1 mm diam) on the disk 153° away from the contact point of the rider. The disk was rotated 153° to bring the contact spot under the electron beam for AES analysis. Electrostatic deflection plates in the electron gun permitted the electron beam (and thus the analyzed spot) to be moved radially in and out of the circumferential track of the contact spot. The Auger spectrum was displayed on an oscilloscope screen with a sweep time of 0.1 second. A typical Auger spectrogram of a tungsten (W) disk after bakeout is shown in figure 2(a). The ordinate is the derivative of the secondary electron energy distribution, while the abscissa is the secondary electron energy. The disk is not clean, and some oxygen (O) and carbon (C) are present on the disk.

SPECIMEN PREPARATION

The disks were lapped and then polished to a mirror finish 5×10^{-6} cm, or 2 μ in., centerline average with 6-micrometer-diameter diamond paste. They were then solvent

cleaned. The last washing was with ethyl alcohol, and the specimens were then placed in the experimental chamber.

The PTFE was high-purity, high-density, research-grade material in the form of 0.952-centimeter- (3/8-in.-) diameter rod. The end was machined to a radius of 0.476 centimeter (3/16 in.) and then abraded smooth with 600 grit polishing paper. Finally, it was washed with ethyl alcohol.

In order to obtain an atomically clean surface, the disk was subjected to argon ion bombardment. This was accomplished by applying a 1000-volt negative potential to the disk at a chamber pressure of 30 to 100 millitorr of argon. Under these conditions a glow discharge surrounded the disk. The argon ions sputtered the surface of the disk and exposed clean metal. Although not shown in figure 1, a retractable metal cup was inserted over the PTFE radius to prevent deposition of metal sputtered from the disk. This cup also prevented the PTFE from being subjected to the "CASING" treatment (crosslinking by activated species of inert gases) (ref. 8). At the termination of sputtering, the argon was pumped out by sorbtion pumps, and then the ion pump was turned on to return the system to a pressure of 1×10^{-10} torr. A spectrogram of a tungsten disk after cleaning is shown in figure 2(b). Note the absence of carbon and oxygen. The system pressure after sputtering was sufficiently low to allow the disk to remain clean for at least 1 hour (as verified by AES).

The disks, after being cleaned by argon ion bombardment, exhibited an Auger spectrum characteristic of the pure metal. Whatever impurities were present in the disk could not have contributed greatly to the interaction of the disk with the PTFE since they were not detected within the limits of sensitivity of the spectrometer (<0.01 monolayer for carbon). Thus, a documented chemically pure metal surface free of all oxides and adsorbed gas (except possibly hydrogen, which is not detectable by AES) was generated.

PROCEDURE

After the specimens were mounted in the chamber, it was baked at 250°C for 12 hours to achieve a base pressure of 1×10^{-10} torr. The disk was then cleaned by argon ion bombardment, usually for 1 hour, and its cleanliness was checked by AES. If free of contaminants, the disk was ready for contacting by PTFE.

For the static contacts the PTFE was pressed onto the disk by the deadweight loading system shown in figure 1. Both initiation and termination of the contact were effected perpendicular to the surface of the disk, care being taken not to introduce tangential motion to the PTFE. After the contact and retraction of the rider from the disk, the disk was rotated 153° to bring the point of contact under the electron beam for AES

analysis. The disk could be accurately positioned by means of an angular scale on the housing of the magnetic rotary feed-through.

For the sliding contact, the PTFE rider was first loaded onto the disk, and then rotation of the disk commenced. The circumferential track of the contact spot was analyzed by AES while the disk was rotating. The presence of PTFE on the metal surface was indicated by the 270-eV carbon and 655-eV fluorine peaks in the Auger spectrogram.

RESULTS

Static Contact

The purpose of these experiments was to determine whether PTFE transfers to a metal surface under static contact and, if such transfer did occur, to explore the conditions under which the transfer took place. A typical series of spectrograms is shown in figure 3 for PTFE contacting an aluminum disk. Figure 3(a) shows the spectrogram of the disk prior to sputter cleaning. Carbon and oxygen are present. After sputtering, the carbon and oxygen are absent, and the 70-eV aluminum (Al) peak can be seen on the left in figure 3(b). After contact of 500 grams for 5 minutes both carbon and fluorine (F) are found in the spectrogram of figure 3(c), and indicate the presence of PTFE on the disk.

The amount of PTFE transferred was independent of the dwell time of the rider on the disk for dwell times between 5 seconds and 5 minutes. The transfer did depend on the loading, however, and became negligible for loads below 100 grams. This dependence is probably due to both the enlargement of the apparent area of contact and the real area of contact by distortion of the rider under compressive loading. No great differences in the amount of PTFE transferred were noted for loads between 250 and 1000 grams, the maximum load used. Repeated contacts with the rider on different parts of the disk were made with essentially the same amount of PTFE observed each time.

The amount of PTFE remaining on the surface of the disk is difficult to estimate with AES. The size of the peaks in the spectrogram is proportional to the abundance of the different species on the surface. However, since the Auger electron yields of the elements are different, each element requires a separate calibration procedure. The size of the carbon Auger peak in figure 3(c) represents somewhat less than a monolayer of carbon, as estimated by experience in our laboratory. However, this is an average figure since the PTFE may be in clumps within the analyzed spot instead of spread out uniformly.

Transfer of PTFE to atomically clean metals by static contact was observed for all materials used. The metals nickel, tungsten, copper, aluminum, iron, and tantalum were used in disk form. Gold and silver films ($\sim 2000 \text{ \AA}$) were deposited on metal disks by ion plating (ref. 9). Gold films were also deposited by thermal evaporation. An Auger spectrogram of a gold (Au) surface before and after contact is shown in figure 4.

The possibility that the transfer of PTFE to metal might be affected by the presence of an oxide film on the metal was investigated by two methods. In the first method, high-purity oxygen was admitted to the chamber after the disk surface had been sputter-cleaned. The oxygen chemisorbed on the surface to monolayer coverage. Static contact was initiated, and again transfer of PTFE was observed. Thus, the presence of a monolayer of chemisorbed oxygen does not affect the transfer observed here.

A more conclusive experiment involved the use of an oxidized aluminum disk. It is known that the natural oxide layer on aluminum is many layers thick. Removing the adsorbed carbon dioxide and carbon monoxide by a short sputtering (20 min) exposed the "clean" aluminum oxide layer (fig. 5(a)). Static contact was initiated, and again PTFE was found on the surface (fig. 5(b)). Thus, PTFE transfers to the oxide of aluminum as well as the clean metal, which implies that the chemical activity of the substrate is not an important factor in the transfer observed in these static contact experiments.

Sliding Contact

There were two objectives in the sliding contact experiments. The first was to use AES to obtain information on the characteristics of PTFE transferred to metals in the sliding process. The second was to investigate the friction of PTFE on well characterized metal surfaces.

Sliding contact was initiated on a tungsten disk. The velocity was 0.07 centimeter per second, and the load was 250 grams. The disk was atomically clean, and its Auger spectrogram is shown in figure 2(b). A transfer film of PTFE is generated on the disk on the first revolution as shown by the Auger spectrogram in figure 6. The carbon and fluorine peaks are much larger than those in the static contact experiments and indicated the presence of larger amounts of PTFE on the surface.

The film is uniform across the track, as indicated by the constancy of the peaks when the deflection plates in the electron gun move the beam across the track. The film is also uniform and continuous along the circumference of the track, as indicated by the constancy of the peaks throughout the first revolution of the disk.

Notice that the tungsten peak is still visible in the Auger spectrum shown in figure 6. This indicates that the film is only a few monolayers thick, since AES is sensitive only

to the first few layers on the surface. Further evidence for this estimate of the thickness comes from the time of less than 20 minutes necessary to remove the film by sputter-cleaning. Since oxide films many layers thick can be removed in 1/2 to 1 hour, the PTFE film should be only a few layers thick.

Information on the structure of the film and its interaction with the substrate may be obtained from the time dependence of the Auger peaks when the disk is stationary and the electron beam impinges on one spot of the surface. In figure 7, two spectra taken 60 seconds apart are exhibited. It can be seen that the fluorine peak has decreased while the carbon and tungsten peaks have grown. The incident 2000-eV electrons have severed the carbon-fluorine bonds in the PTFE, and the fluorine has desorbed from the surface. The carbon remains behind on the surface. With the departure of the fluorine, Auger electrons from the carbon and tungsten beneath the fluorine can leave the surface, enter the analyzer, and cause growth of these peaks. Exposure of the surface to the electron beam for about 1 minute resulted in complete disappearance of the fluorine peak (fig. 7(b)).

To realize the significance of these results for the interaction between PTFE and the metal substrate, it is necessary to consider some general characteristics of electron-induced desorption of surface species on metals. It has been established that the cross section (desorption probability) for electron desorption of chemisorbed surface species, $\sim 10^{-20}$ square centimeter, is orders of magnitude smaller than the ionization and excitation cross sections for free atoms and molecules, $\sim 10^{-16}$ square centimeter (refs. 10 and 11). It has been proposed that the small cross section is due to the reformation of the bond initially broken by the bombarding electrons by tunneling of electrons from the metal to the excited atom before it can leave the surface. Such tunneling occurs only if the surface species is in intimate electronic contact with the metal, for example, chemically bonded to it.

The cross section for fluorine desorption may be calculated from the time dependence of the fluorine peak and the equation $S(t) = S(0) \exp(-\sigma J_0 t)$. Here $S(t)$ is the magnitude of the fluorine peak at time t , σ is the cross section for electron-induced desorption of fluorine, and J_0 is the incident electron flux. A value of $\sigma \sim 5 \times 10^{-18}$ square centimeter is obtained from the decay of the fluorine peak.

This value is much larger than that appropriate for species chemically bonded to the metal, and the conclusion is that there is no chemical interaction between the fluorine in the PTFE and the metal substrate. The value of the cross section is smaller than that for excitation and ionization of free molecules, and this is probably a consequence of the multilayer structure of the film. That is, a fluorine ion detached from a carbon ion in the interior of the film is likely to reform a bond with another carbon ion in the film, and the result will be a cross section for fluorine desorption smaller than that for an isolated PTFE chain.

In contrast to the desorption of fluorine by the electron beam, the carbon remains on the surface. This behavior is consistent with the polymeric structure of PTFE, which is depicted in figure 8. While there is one chemical bond between fluorine and carbon, the carbon atoms have four bonds, two with other carbons and two with fluorine. Since the two bonds retaining the carbon in the chain must both be broken for it to be desorbed, such desorption is a highly unlikely event with the electron beam current densities employed in this report.

It thus appears from observations with AES that the transfer film is indeed a polymeric chain and that the fluorine in the film has no chemical interaction with the metal.

To further investigate the sliding of PTFE on well characterized metal surfaces, the coefficient of friction was measured. Under the conditions of a 250-gram load, a sliding velocity of 0.07 centimeter per second, and an atomically clean tungsten disk, the coefficient of friction was 0.08 during the first revolution of the disk. This value for PTFE sliding on clean tungsten is the same value obtained for PTFE sliding on glass and PTFE on metals in air (ref. 2).

To assess the effect of surface contaminants or films on the friction of PTFE, the disk was allowed to continue for a second traversal. The PTFE was then sliding on its own transfer film. It was found that the friction force was unchanged upon this second traversal. It thus appears that for PTFE sliding in vacuum neither the chemical activity of the substrate nor the presence of contaminant films influences the force of friction.

Although the friction was independent of the chemical constitution of the substrate, the mechanical strength of the disk could greatly influence the sliding behavior of PTFE. An interesting illustration is furnished by sliding PTFE on aluminum in vacuum with a 500-gram load at a sliding velocity of 1 centimeter per second. The result obtained after 26 revolutions of the disk is shown in figure 9. Identical results are obtained with the naturally occurring oxide film either present or sputtered away. Note that aluminum chips are covering the surface, and there is present a curl of metal under the rider. The PTFE film transferred on the first revolution was removed by this scoring process.

Apparently wear fragments of aluminum are produced in the sliding process. These fragments lodge in the PTFE rider, work harden, and then serve to actually machine the surface. This machining phenomenon is also observed in air but to a much lesser extent. This difference in air and vacuum is probably due to the reformation of the oxide film in air so that the metal tipped rider must dig into the harder oxide rather than the soft aluminum metal when in vacuum.

The plucking of wear fragments from the substrates was also observed for PTFE sliding on copper and gold film ion-plated on tungsten. However, because of the higher strength of the substrate, there was little machining. These observations point to the danger of sliding PTFE on soft metals such as copper, aluminum, or gold. Once wear particles lodge in the rider, the coefficient of friction no longer reflects any fundamental

interaction between PTFE and the metal but rather the machining or plowing action of the metal-tipped PTFE rider. This is illustrated in figure 10, in which the coefficient of friction of PTFE on aluminum and tungsten is plotted. Initially, the coefficient of friction of 0.08 is the same for both disks, in accord with previous observations. However, as the rider picks up wear fragments from the aluminum disk, the friction rises to much higher values and becomes erratic. The friction of the tungsten disk is very smooth and is unchanged upon a second revolution of the disk.

DISCUSSION

Auger emission spectroscopy has been used to observe PTFE transfer to metals following tensile fracture of static contact. It is important to understand the adhesive mechanism that is responsible for this transfer.

Consider first the possibility of the formation of chemical bonds (ref. 6). The ends of the polymer chains in the rider probably consist of unsatisfied carbon bonds (i.e., active radicals). Pressing the rider onto the disk would establish intimate contact of the PTFE with the metal at the interfacial junctions with the formation of carbon-metal bonds. These carbon-metal interfacial bonds may be expected to be stronger than the carbon-carbon covalent bonds in the PTFE. Tensile fracture of the junctions should then result in fracture of the cohesive bonds in the PTFE and leave PTFE on the surface, as observed.

Such an adhesion mechanism, however, would be expected to be chemically specific. That is, the transfer should depend on the chemical activity of the substrate. Atomically clean metal surfaces such as tungsten or aluminum are indeed very active and will form chemical bonds with carbon. However, in this study after the surface was passivated with a monolayer of oxygen, transfer was observed. Also, copper, gold, and aluminum oxide are chemically inactive, and transfer would not be expected to occur. Since the transfer is observed whatever the chemical constitution of the substrate, an explanation in terms of chemical bond formation alone is unlikely and a more general bonding mechanism must be sought.

The possibility that the observed transfer may be an artifact of the method of preparation of the PTFE rider must be considered. Preparation of the specimens by abrasion may have created a highly disorganized surface region with many small islands or strands of PTFE that lack covalent bonding or through-going chains to the main body of the polymer. Such weak boundary layers have been considered to be responsible for the weakness of polymer bonding to substrates. The absence of covalent bonding to the main body of the polymer makes these regions vulnerable to detachment by general physical or van der Waals forces from the metal. This mechanism is expected to be independent

of the chemical constitution of the substrate, as observed. However, the number of these islands on the specimen should be depleted as the number of contacts made increases. Thus, a continuous decrease in the amount of polymer transferred would be observed as repeated contacts are made. Such a continuous decrease is, however, not observed. Thus, the transfer cannot be considered an artifact of the method of preparation of the polymer specimen.

It thus appears that the observed transfer is due to true cohesive separation in the polymer. Van der Waals forces have usually been considered to be responsible for bonding of polymers to substrates (ref. 12). Presumably they are also responsible for the transfer observed here. These forces are present between all atoms and are not as strongly a function of the particular elemental species involved as with chemical activity. Although these forces, in themselves, are not as strong as the covalent bonds of the polymer, the separation in the polymer can probably be explained in terms of the fracture mechanics of the interfacial junctions. This is the manner in which cohesive fracture of polymer adherends is usually considered (ref. 13).

In this connection the relevance of AES for the general field of polymer adhesion should be indicated. In the field of tribology it is important to identify the locus of failure of a polymer-metal composite that is separated in a tensile or peel test (ref. 13). The separation is said to be "interfacial" if no polymer can be detected on the metal. The metal has usually been examined with microscopic or spectroscopic tools that have less surface sensitivity than AES. Postseparation examination with AES, with its sensitivity to fractional monolayer concentrations, may reveal, as suspected by some, that interfacial separation never occurs and some polymer always remains on the metal.

The sliding experiments here have shown that the coefficient of friction of PTFE on tungsten in ultrahigh vacuum is the same whether the rider slides on atomically clean tungsten or on its own transfer film. The coefficient of friction of 0.08 is the same as that for PTFE sliding on itself or clean glass in air for equivalent loading and sliding velocity. It thus appears that the coefficient of friction is independent of chemical constitution of the substrate and ambient environment for these loads and speeds. This behavior is in sharp contrast to the behavior of most systems in which chemistry and environment are all-important determinants of friction. This is further confirmation of the uniqueness of PTFE as a friction and wear material. Certainly the usual concepts employed in the adhesion theory of friction (refs. 3 and 4) must be modified to deal with such a situation.

Makinson and Tabor (ref. 2) have proposed a model for the friction of PTFE that employs two physical mechanisms. The first is the traditional one of adhesion between the polymer and the substrate. The second is tangential motion of the contact which results in the drawing out of lamellae of polymer from the body of the rider. The friction force thus results from the force necessary to draw these lamellae out and is not

due to the traditional mechanism of fracture in shear of adhesive junctions between the contacting bodies. Based on this view, as long as there is sufficient initial adhesion to allow the drawing process to proceed, the friction should be independent of the environmental and chemical constitution of the substrate. The sliding experiments discussed in this report together with the experiments of Makinson and Tabor are in accord with this prediction.

The other part of the sliding mechanism, the adhesion necessary to anchor the lamellae, has up to now received only circumstantial support. Makinson and Tabor considered the adhesion "very strong," whereas Steijn noted that it needs to be only strong enough to permit the drawing of lamellae to proceed. Here it has been shown that there is strong enough adhesion initiated by mechanical static contact to allow fracture in the PTFE. This adhesion would then be strong enough to anchor the lamellae. The adhesive transfer observed by static contact is, like the friction force, independent of the chemical constitution of the substrate. Thus, an important aspect of the lamellae-drawing model of the friction of PTFE has been confirmed.

It is now of interest to compare the mechanism of friction of PTFE with that for those materials that obey the adhesion theory of friction. The friction of these latter materials arises from the force necessary to break adhesive junctions, the strength of which depends on the chemical constitution of the substrate. These junctions are constantly being broken and reformed during sliding, so that the coefficient of friction furnishes information on the adhesion between the sliding bodies. With PTFE, on the other hand, the friction force is due to the drawing of lamellae from the body of the rider. Since there always seems to be sufficient adhesion to anchor the lamellae, the coefficient of friction is the same for all hard substrates and gives little information about the adhesion between PTFE and the substrate. Further information on adhesion must come from static contact experiments such as described in this report or from peel or tensile tests of PTFE-metal couples.

As a final observation on the adhesion mechanism, it should be recognized that the adhesive force is strong enough to generate wear particles from soft metal substrates. This observation may lead to further information on the strength of adhesion by studying the wear process as a function of the strength of the metal substrates. Such a study would be complimentary to the studies involving peel or tensile tests of melt-formed joints in that the wetting process is not involved in the formation of the adhesive junction.

SUMMARY OF RESULTS

The new technique of Auger emission spectroscopy has been used here to detect polytetrafluoroethylene on metal surfaces in ultrahigh vacuum. Concentrations of poly-

mer of less than one monolayer were observed.

AES has shown that PTFE transfers to metal surfaces following static compressive contact. There is sufficient adhesion of PTFE to the substrate to allow separation to occur in the PTFE. This adhesive transfer appears to be independent of the chemical constitution of the metal and the presence of oxide films on the surface. It thus appears that the usual van der Waals forces are responsible for the separation within the polymer.

For PTFE in sliding contact with a hard metal surface a uniform continuous film of PTFE only a few atomic layers thick is detected by AES. The transfer film is generated on the initial pass of the PTFE over the surface. The fluorine in the film is rapidly desorbed by the 2000-eV, 70-microampere electron beam, and this desorption shows that the fluorine in the film has no chemical interaction with the metal. The coefficient of friction of PTFE sliding on atomically clean or oxidized metal in ultrahigh vacuum was 0.08 at a load of 250 grams and a sliding velocity of 0.07 centimeter per second. This coefficient of friction is the same for PTFE sliding on glass in air. The friction of PTFE appears to be independent of the chemical constitution of the substrate. These results furnish support for the Makinson-Tabor lamellae-drawing picture of the sliding of PTFE.

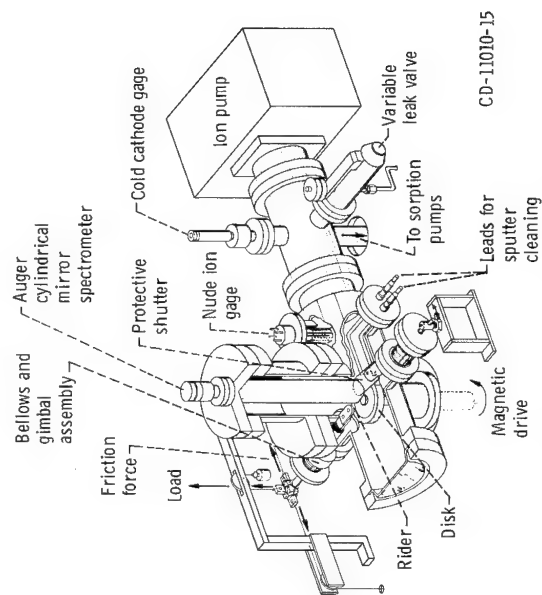
PTFE sliding on soft metals can generate wear particles of the metal that lodge in the PTFE and machine the substrate. Such machining removes the transfer film initially generated. The generation of wear fragments of metal further characterizes the adhesion of PTFE to metals.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, July 18, 1972,
502-01.

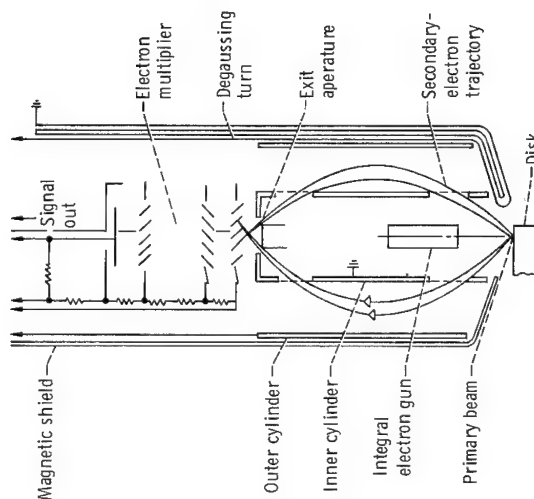
REFERENCES

1. Chang, Chuan C.: Auger Electron Spectroscopy. *Surface Sci.*, vol. 25, no. 1, Mar. 1971, pp. 53-79.
2. Makinson, K. Rachel; and Tabor, D.: The Friction and Transfer of Polytetrafluoroethylene. *Proc. Roy. Soc. (London), Ser. A*, vol. 281, no. 1384, Aug. 25, 1964, pp. 49-61.
3. Steijn, R. P.: The Sliding Surface of Polytetrafluoroethylene: An Investigation with the Electron Microscope. *Wear*, vol. 12, 1968, pp. 193-212.

4. Bowden, Frank P.; and Tabor, David: The Friction and Lubrication of Solids. Part I. Clarendon Press, 1950.
Bowden, Frank P.; and Tabor, David: The Friction and Lubrication of Solids. Part II. Clarendon Press, 1964.
5. Buckley, Donald H.: Friction, Wear, and Lubrication in Vacuum. NASA SP-277, 1971.
6. Brainard, William A.; and Buckley, Donald H.: Adhesion of Polymers to Tungsten as Studied by Field Ion Microscopy. NASA TN D-6524, 1971.
7. Buckley, Donald H.; and Pepper, Stephen V.: Elemental Analysis of a Friction and Wear Surface During Sliding Using Auger Spectroscopy. NASA TN D-6497, 1971.
8. Hansen, R. H.; and Schonhorn, H.: A New Technique for Preparing Low Surface Energy Polymers for Adhesive Bonding. J. Polymer Sci., Pt. B, vol. 4, no. 3, 1966, pp. 203-209.
9. Spalvins, Talivaldis; Przybyszewski, John S.; and Buckley, Donald H.: Deposition of Thin Films by Ion Plating on Surfaces Having Various Configurations. NASA TN D-3707, 1966.
10. Menzel, Dietrich; and Gomer, Robert: Desorption from Surfaces by Slow-Electron Impact. J. Chem. Phys., vol. 40, no. 4, Feb. 15, 1964, pp. 1164-1165.
Menzel, Dietrich; and Gomer, Robert: Desorption from Metal Surfaces by Low-Energy Electrons. J. Chem. Phys., vol. 41, no. 11, Dec. 1, 1964, pp. 3311-3328.
11. Musket, Ronald G.: Auger Electron Spectroscopy Study of Electron-Impact Desorption. Surface Sci., vol. 21, 1970, pp. 440-442.
12. Schonhorn, Harold: Adhesion. Encyclopedia of Chemical Technology. Second ed. Interscience Publ., 1971, Supp., p. 16.
13. Cherry, B. W.; and Holmes, C.: Mechanics of Failure of Adhesive Joints. Aspects of Adhesion. Vol. 6. D. J. Alner, ed., CRC Press, 1971, p. 80.

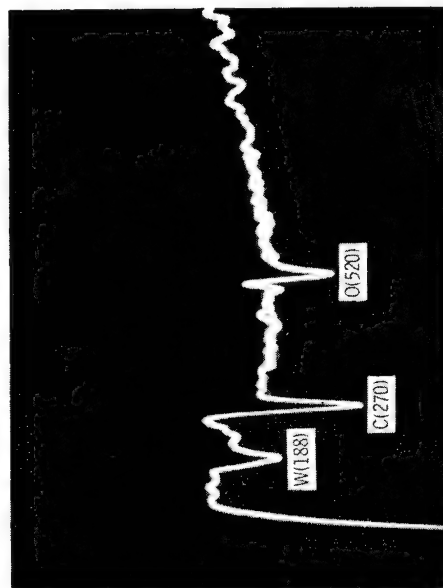


(a) Friction apparatus with Auger spectrometer.

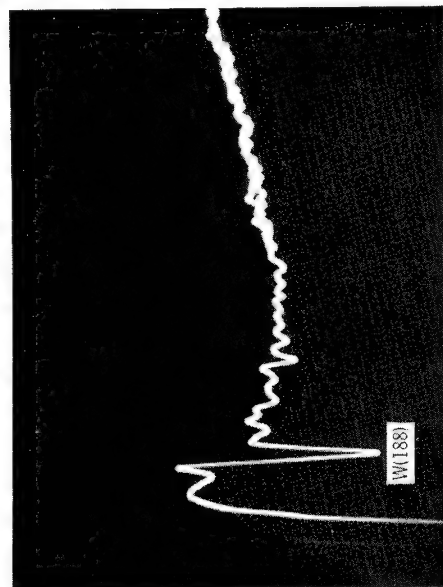


(b) Auger cylindrical mirror analyzer.

Figure 1. - Experimental apparatus.



(a) AFTER BAKEOUT AT 250° C FOR 12 HOURS.



(b) AFTER SPUTTER CLEANING FOR 1 HOUR.

Figure 2. - Auger spectrum of tungsten disk.

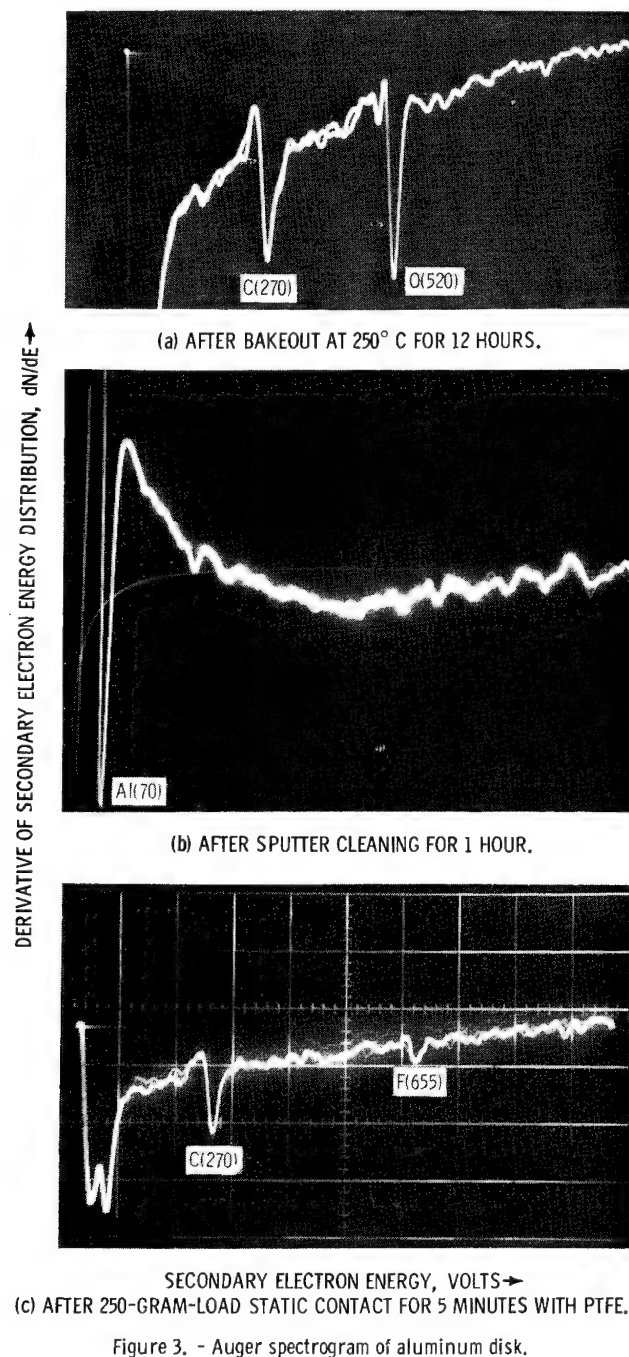


Figure 3. - Auger spectrogram of aluminum disk.

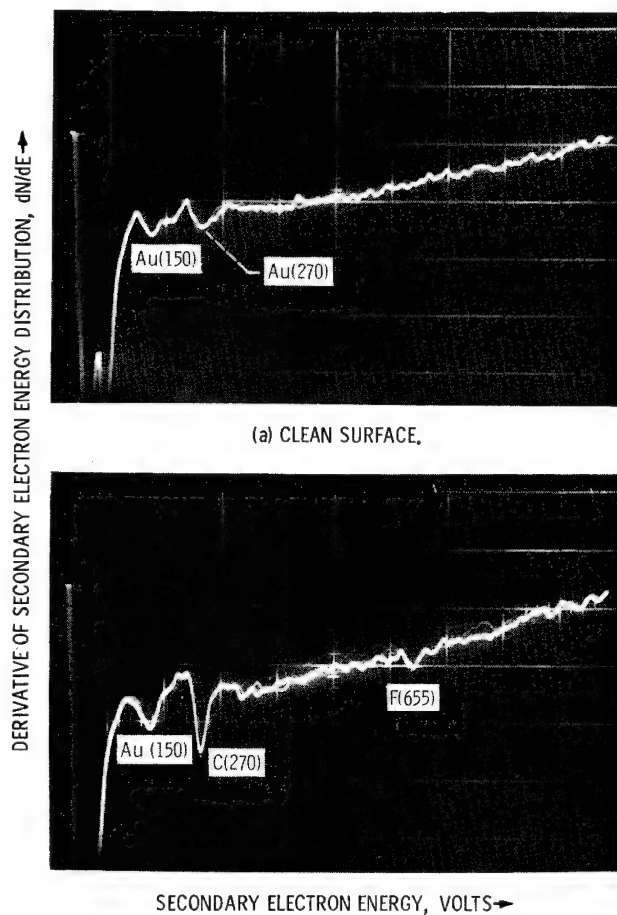
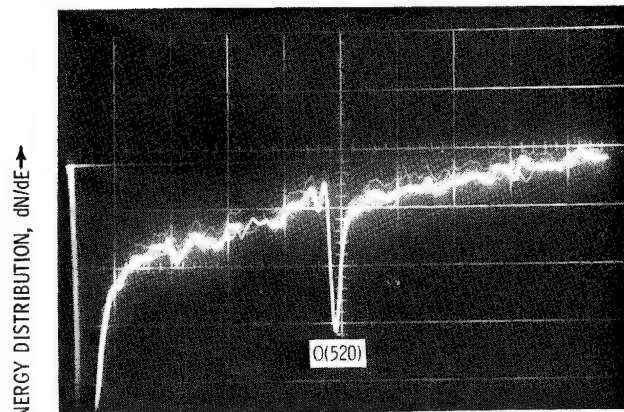
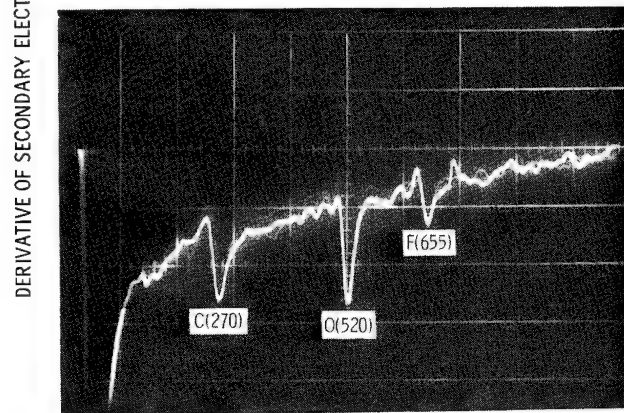


Figure 4. - Auger spectrogram of gold surface.



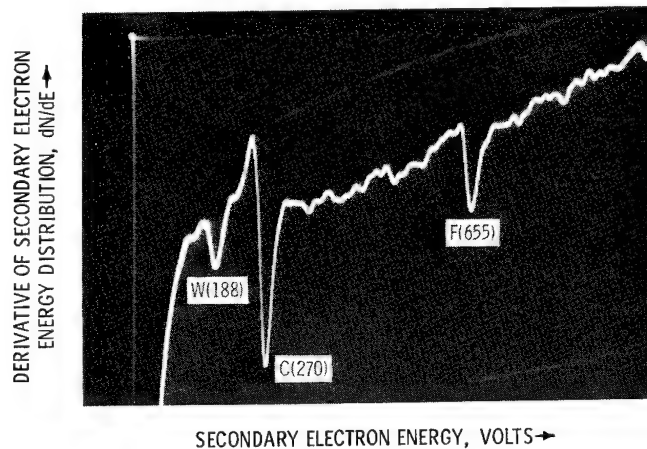
(a) AFTER SPUTTER CLEANING FOR 20 MINUTES.



SECONDARY ELECTRON ENERGY, VOLTS →

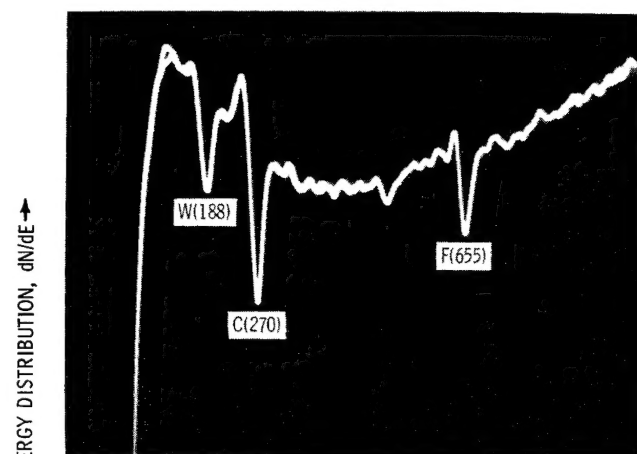
(b) AFTER 500-GRAM-LOAD STATIC CONTACT FOR 5 MINUTES WITH PTFE.

Figure 5. - Auger spectrogram of aluminum surface.

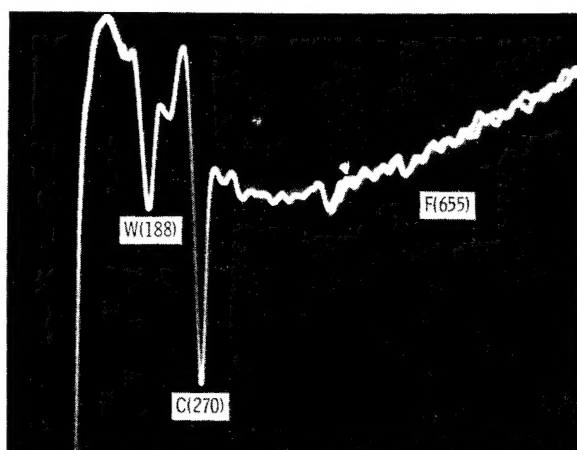


SECONDARY ELECTRON ENERGY, VOLTS →

Figure 6. - Auger spectrogram of tungsten disk after 1 pass of PTFE rider. Load, 250 grams; sliding velocity, 0.07 centimeter per second.



(a) DISK WITH PTFE FILM GENERATED BY 100-GRAM-LOAD SLIDING AT VELOCITY OF 1 CENTIMETER PER SECOND.



(b) SAME SPOT ON DISK AS IN (a) AFTER 1-MINUTE TIME INTERVAL; 70-MICROAMPERE BEAM CURRENT.

Figure 7. - Auger spectrogram of tungsten disk.

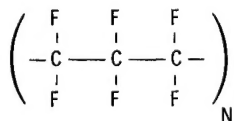
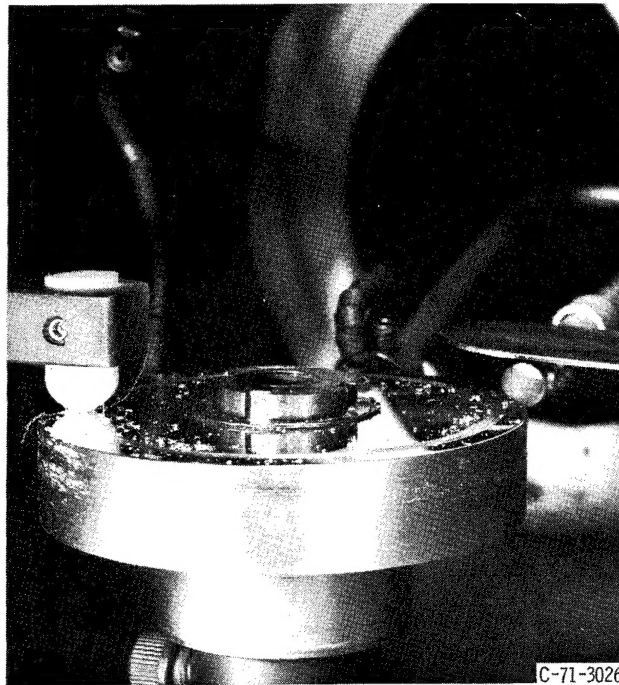
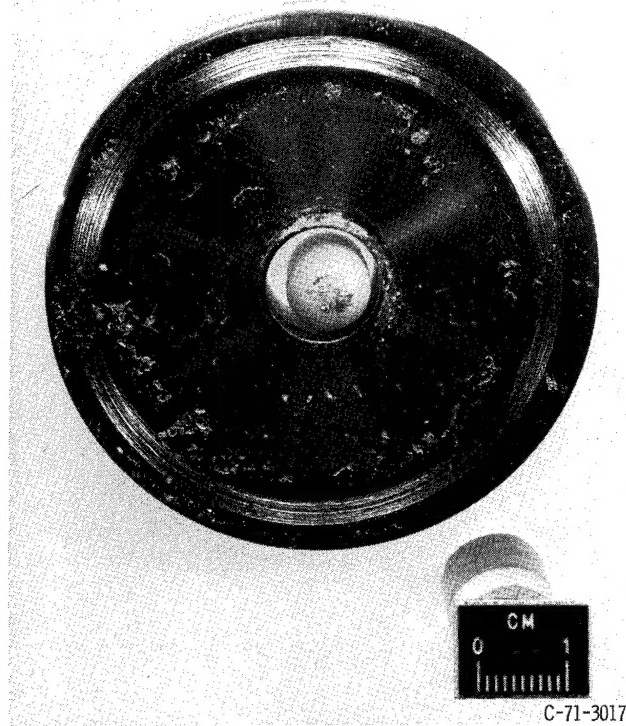


Figure 8. - Chemical structure of PTFE.



(a) Rider and disk with Auger spectrometer removed.



(b) Top view of disk.

Figure 9. - PTFE rider on aluminum disk. Surface of disk is covered with aluminum chips, and PTFE rider has aluminum chips imbedded in it.
 - Load, 500 grams; sliding velocity, 1 centimeter per second; 26 revolutions in vacuum.

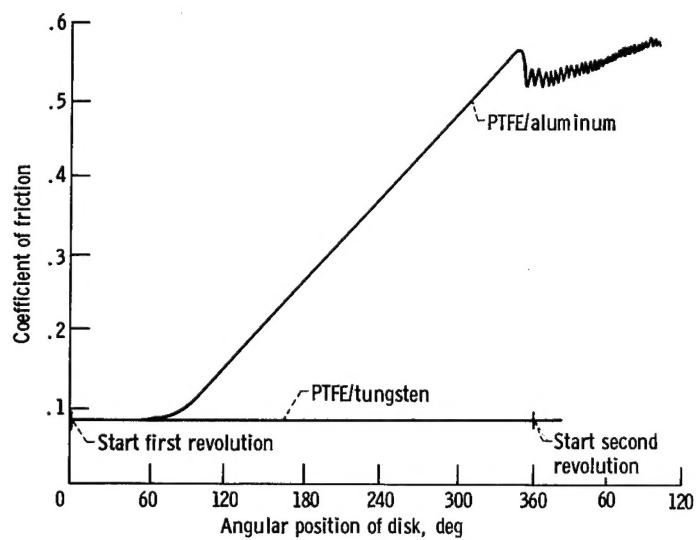


Figure 10. - Coefficient of friction of PTFE on aluminum disk and tungsten disk in vacuum. Sliding velocity, 0.07 centimeter per second; load, 250 grams.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE \$300

**SPECIAL FOURTH-CLASS RATE
BOOK**

POSTAGE AND FEES PAID
NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION
451



008 001 C1 U 18 720929 S00942DS
DEPT OF THE ARMY
PICATINNY ARSENAL
PLASTICS TECHNICAL EVALUATION CENTER
ATTN: SMUPA-VP3
DOVER NJ 07801

3401

POSTMASTER: If Undeliverable (Section 158
Postal Manual) Do Not Return

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons. Also includes conference proceedings with either limited or unlimited distribution.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include final reports of major projects, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION OFFICE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington, D.C. 20546